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THE NATURE OF CERTAIN ALUMINIUM COMPOUNDS IN THE
SOIL AND THEIR INFLUENCE ON AMMONIFICATION
AND NITRIFICATION

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
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THE NATURE OF CERTAIN ALUMINIUM SALTS IN THE SOIL AND
THEIR INFLUENCE ON AMMONIFICATION AND NITRIFICATION

By

IRVING A. DENISON

I. I N T R O D U C T I O N

That soluble salts of aluminium are present in acid soils in considerable quantities, and that these salts may be largely responsible for soil acidity are conclusions that have been reached by several investigators. The literature on aluminium in its relation to soil acidity has been fully reviewed by Mirasol (10) so that no attempt need be made in this paper to treat the subject historically, especially in view of the fact that the problem to be discussed deals in part with the influence of aluminium salts on bacterial activity, on which subject little work has been reported. References to the literature will be made from time to time as they bear directly upon the particular topic under discussion.

The toxicity of soluble aluminium salts toward farm crops has been clearly demonstrated by Hartwell and Pember, (5) Abbott, Conner and Smalley, (1) Mirasol, (10) and by the writer in some preliminary work, which in view of its agreement with what has been reported need not be considered further. However, there does not appear to be such definite information regarding the effect of these salts upon such important bacterial processes as ammonification and nitrification. In view of the fact that the hydrolysis of the sulfate, chloride and nitrate of aluminium produces a strongly acid medium, it would be expected that the nitrifying organisms would be affected adversely by the presence of these salts in the soil. Furthermore, since it has been maintained by some

investigators and particularly by Mirasol, that the origin of soluble aluminium salts in the soil is for the most part to be ascribed to bacterial activity, it became desirable in planning this work to study this factor also.

II. THE NATURE OF CERTAIN ALUMINIUM COMPOUNDS IN THE SOIL

Before attempting experimental work involving a study of bacterial activity as influenced by aluminium salts, it was deemed essential to investigate in some detail the exact nature of the aluminium compounds of the soil which might be involved in the problem under consideration. Merely to group all the aluminium compounds that might be extracted from the soil under a single head, namely, as being toxic to plant growth, seemed from a consideration of the widely differing nature of the aluminium compounds concerned to be wholly unwarranted. It would be well then to review very briefly the opinions that are held with respect to the character and origin of these compounds before entering into a discussion of the experimental work to be reported.

Theories of the Formation of Soluble Aluminium in Soils

Probably one of the first investigators to give attention to the presence of aluminium in the soil from the standpoint of soil acidity was Veitch (15), who, in his study of the Hopkins' method for the determination of soil acidity, attributed the acidity of the soil extract to hydrolyzed aluminium salts which had been formed by the replacement of the aluminium in aluminosilicates by the basic ion of the neutral salt solution used as an extractant in this determination. Truog (14) holds much the same view, stating that the treatment of an acid mineral soil with a salt solution results in the exchange of an equivalent amount of iron and aluminium for the base taken up. The iron and aluminium go into solution as salts and since they are strongly hydrolyzed in solution, they

enter into the titration much the same as an equivalent amount of acid. The conception that the presence of these salts is to be ascribed to true displacement by the basic ion of the salt solution receives further support according to Truog from the fact that acetates bring aluminium and iron into solution as well as salts of the stronger mineral acids. It is improbable in his opinion that the dilute acetic acid formed by removal of the base would dissolve iron and aluminium compounds to saturation.

A second theory to explain the presence of aluminium in neutral salt extracts of soil is that held by Parker (11), who assumes that aluminium is brought into solution by a side reaction of free acid formed by the removal of the basic ion of the salt solution by selective adsorption. Knight (9) takes much the same view, asserting, however, that the basic ion is removed to make up the deficiency of bases in the acid soil rather than by physical adsorption. The mineral acid thus formed from the acid ion of the salt solution then attacks insoluble aluminium bringing it into solution as the hydroxid and not as the salt of the mineral acid as is assumed by the replacement of bases theory. This is a very important point, and it is the starting point of much of the work that will be reported later.

In addition to the two theories that have been mentioned to account for the rise of soluble aluminium compounds in the soil, attention should be directed to a third, namely, the biochemical origin of soluble aluminium. Abbott, Conner, and Smalley in 1913 (1) reported the presence of aluminium nitrate in a peat soil and attributed its rise to nitrification taking place in the absence of a more suitable base than aluminium. This idea has been developed recently by Mirasol. From the work by Ames and Boltz (2) it would appear that aluminium may be brought into solution also as the sulfate in the process of sulfonation.

There have been presented then three explanations of the existence of

soluble aluminium in the soil: first, that it is brought into solution by replacement of bases from alumino-silicates; second, that it is produced by the action of acid formed by withdrawal of the base from a neutral salt solution; third, that it has its origin in the normal processes of nitrification and sulfification.

An understanding of which of these three processes that actually occurs or whether they all take place in the soil, while of considerable value, is of secondary importance as compared to a knowledge of the actual chemical compound in which aluminium enters and exists in the soil solution. To illustrate, if aluminium salts of the mineral acids are constantly being produced in some acid soils, the theory that has now been fully accepted by many, that active aluminium is an important factor in acidity would appear to receive added confirmation. If, however, the soluble aluminium of the soil is present more likely as the hydroxide, as the work of Knight indicates, and not as salts, then aluminium ceases to be the important factor that it is claimed to be and becomes not more than a measure of acidity, the actual cause of which lies much deeper, but which is as yet not understood.

The Presence of Soluble Aluminium Hydroxide in Soil Extracts

A review of the work of Knight, to which reference has been made, may serve to bring out more clearly the point that has just been mentioned. In his study of the Hopkins' method for soil acidity, Knight found that the aluminium present in the potassium nitrate extract of an acid soil was only slightly less than enough to account for the total acidity of the extract as measured by titration with standard alkali. Basing his reasoning on the work of Blum (3), who showed that aluminium hydroxide is completely precipitated before the hydrogen ion concentration of the solution reaches pH 7; and conversely must pass into

solution when the hydrogen ion concentration rises above this value, Knight inferred that the aluminium which he determined in the extract was present as the hydroxide. The extract was then subjected to dialysis with the result that none of the aluminium contained within it diffused through the membrane; whereas three-fourths of the total acidity of the extract was found to have diffused. On neutralization of the contents of the collodion flask aluminium hydroxide was precipitated. The logical interpretation of the result of this experiment is that the aluminium extracted from the soil by a neutral salt solution is present not as the easily diffusible salt, the nitrate in this case, but as soluble aluminium hydroxide.

Additional support of this contention is provided by the investigations of Rose, (12) from which it appears that precipitated aluminium hydroxide passes readily into the hydrosol condition in the presence of very weak acid, namely 4 percent acetic acid and N/20 to N/35 hydrochloric or nitric acid. The author explains this formation of hydrosols as being due to the forming of a series of hydrated oxides, those hydrates containing the largest number of molecules being produced first. In studying the solubility of aluminium hydroxide in acetic acid, Rose found that hydrates having the formulas $\text{Al}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ were produced first, swelling up and setting as gelatinous masses. With the addition of more acetic acid $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ to $\text{Al}_2\text{O}_3 \cdot 2.75 \text{H}_2\text{O}$ formed, giving only weakly opalescent solutions. As soon as the degree of hydration passed below the last value with additional acid, a hydrosol no longer formed and normal aluminium acetate resulted.

It would seem then that this action of weak acids on aluminium hydroxide might easily explain the presence of soluble aluminium in the soil. The weak acid of the soil or the acid produced by the withdrawal of the basic ion from a salt solution reacts with colloidal aluminium hydroxide with the production

of a solution to all intents and purposes perfectly clear, but containing aluminium in a form which will not pass through a semi-permeable membrane. That there are considerable quantities of aluminium hydroxide in soils is the conclusion reached by Mirasol after a review of the literature, so that there seems to be no reason why the conversion of aluminium hydrogels to hydrosols should not take place within the soil. It should be mentioned in this regard that according to the work of Rose, the aluminium hydroxide need not be in the gelatinous condition, i.e., as when precipitated by ammonium hydroxide, in order to enter the sol state. Perfectly dry aluminium hydroxide will pass readily into the sol provided that it has not been dried at too high a temperature. The application of this principle to soil conditions is, of course, that the hydroxide in the soil need not be in the plastic condition associated with wet clay in order to form the sol but it may be simply as a finely-divided powder. In summary, if this principle of the reversibility of aluminium hydrogels to hydrosols obtains within the soil, aluminium passes into the soil solution not as the diffusible salt of an acid but as the indiffusible hydroxide. Not only does this theory appear plausible but it offers a ready explanation for the fact that Knight was unable to bring about diffusion of aluminium from a colloidal flask. The tendency, however, of increasing soil acidity would be eventually to convert aluminium hydroxide to soluble salts of aluminium.

Data from a totally different source tends toward substantiation of the theory that has just been proposed. Reference is made to the extremely large quantities of aluminium which Mirasol succeeded in leaching from three acid soils by extracting with potassium nitrate and water until the last portions of the percolate showed in each case no titratable acidity. After drying, the soils were analyzed for aluminium, the difference in the aluminium content of the leached and unleached soil being taken as the active aluminium normally

to be found in the soils. The table below has been compiled from the results of analysis as reported by Mirasol.

Table I:- Analysis of aluminium in soil, potassium nitrate and water extracts. Results expressed pounds per acre. (2,000,000 pounds to depth of 6 $\frac{2}{3}$ inches)

Soil	Total aluminium in original soil	Aluminium in pot- assium nitrate extract	Aluminium in water extract
	p.p.a.	p.p.a.	p.p.a.
Gray Silt Loam	121,000	54,000	21,400
Yellow Gray Silt Loam	151,200	90,600	33,400
Yellow Silt Loam	149,400	75,600	32,200

Now it is obvious that the enormous quantities of aluminium represented in the above table as having been extracted from the soils could not have been completely combined with nitrate, chloride, sulfate and phosphate ions, as the total of these acid ions could account for but a small fraction of the aluminium. It is conceivable that extraction of the soils with potassium nitrate may have converted aluminium combined as aluminium silicates into aluminium nitrate through replacement of aluminium by potassium, but no such explanation is offered to explain the high quantities of aluminium in the water extract.

Finally, with respect to the quantity of soluble aluminium in soils, it is necessary to state that no analyses of water extracts of soils for aluminium that have come to the attention of the writer have revealed more than insignificant quantities of aluminium. Typical of such analyses is the data reported in Table II, which have been reproduced from the work of Kelley (8).

Table II:- Soluble alumina in water extracts of soils as reported by Kelley. Extraction of air-dry soil.

Soil No.	Alumina	Soil No.	Alumina	Soil No.	Alumina	Soil No.	Alumina
	p.p.m.		p.p.m.		p.p.m.		p.p.m.
74	11.1	292	16.6	416	17.6	428	4.4
164	7.5	290	19.1	417	15.3	426	2.9
9	4.8	405	7.6	406	10.3	448	4.9

Calculated on the basis of elemental aluminium the results would be one half only of the figures given. These soils, although containing bases, react acid.

Having established the nature of the compounds in which the soluble aluminium of the soil exists, it would then be desirable to throw further light on the conditions surrounding the rise of these compounds in the soil, particularly of the salts such as the nitrate and sulfate. Several investigators have reported the formation of the nitrate and sulfate in the soil, namely Abbott, conner and Smalley (1) Ames and Boltz, (2) and Ruprecht and Morse (13), and it seems probable that these salts exist in very acid soils in quantities sufficient to exert a toxic effect; yet some doubt exists as to whether the salts were actually present in the quantities reported. At any rate the soluble hydroxide could have been produced under the conditions of the experiments, and it would have to be eliminated as a factor before the soluble aluminium which is produced in nitrification, sulfonation and by the application of ammonium sulfate could be said to be combined with the particular acid concerned. In other words, the increased acidity that is produced in these processes could readily convert aluminium hydroxide to the hydrosol, but as soon as the acidity of the soil reaches a sufficiently high point aluminium nitrate and sulfate are certain to be produced.

III. EXPERIMENTAL

The Nature of the Problem

It is evident from the foregoing discussion that considerable doubt exists as to the exact form in which soluble aluminium occurs in the soil; whether it occurs principally as salts of the soil acids, or whether it is to be found in greater quantity in the form of the soluble hydroxide. Clearly until definite information which points in one way or the other is obtained, little

progress of a bacteriological nature could be made. If aluminium salts do not occur in soils in appreciable quantities, then their influence on bacterial activity, while of considerable scientific interest is hardly of practical value from the standpoint of soil fertility. Consequently, before attempting bacteriological work definite information as to the form in which aluminium salts occur in the soil must be secured.

What is needed then is some means of differentiating quantitatively between aluminium as salts and aluminium as the hydroxide. Dialysis at once suggests itself as the most logical means of effecting this result. With respect to the completeness of separation of diffusible aluminium salts from the hydroxide by dialysis, there can be no question, as Jones, (6) reviewing the work of Graham on dialysis of aluminium chloride from aluminium hydroxide, states that the aluminium chloride dialyzed without undergoing decomposition, and that no trace of chloride was to be found in the alumina after the process had been completed. This statement also removes any doubt as to whether the aluminium salts in passage through the membrane are dissociated into the acid ion and aluminium hydroxide. Furthermore, it is a principle of dialysis that the membrane itself has no influence on the rate of diffusion of molecules sufficiently small to pass through the membrane. Therefore, since aluminium salts diffuse rapidly like any other electrolyte no difficulty should be experienced in effecting complete separation of the salts from the hydroxide. Determination of aluminium after dialysis in the diffused portion and in that portion remaining within the membrane gives at once the quantity of both forms of aluminium in the extract. A method of differentiation between the forms of aluminium having been found, it becomes merely a question of preparing natural salt extracts of several acid soils and subjecting them to dialysis.

If aluminium salts are to be found in acid soils, then a complete extracting of the water soluble acidity of these soils must reveal the presence of

aluminium in the extract, since the nitrate, chloride, and sulfate of aluminium are easily extractable by water.

Experimental work carried out along the lines that have been suggested should determine the quantity of aluminium as salts of the mineral acids, likely to be found in acid soils. It would then be necessary to ascertain whether the rise of soluble aluminium in the soil is to be ascribed to the replacement of aluminium by other bases or whether it has a biochemical origin or whether both processes may account for its presence. The incubation of aluminium in solution cultures of nitrifying organisms containing no free base but aluminium, and subsequent determination of nitrate and aluminium in the cultures would indicate whether aluminium is rendered soluble in nitrification, or in other words, whether it may serve as the base in nitrification. Likewise incubation of soil with sulfur and dialysis of the extract should show whether soluble aluminium may be formed in sulfonation.

Having determined the quantity of soluble aluminium salts in acid soils, an experiment would be carried out to ascertain whether ammonification and nitrification might be inhibited in such concentrations of salts. Incubation of soil with several concentrations of the aluminium salts likely to be found in the soil should answer this question.

If inhibition of nitrate production should result from the toxicity of aluminium it would be desirable to know what fertilizer material or soil amendment would be most effective in rendering the aluminium inactive.

Description of the Soils Used

The soils studied in this investigation were the same as those used by Mirasol in his work to which several references have been made. The chemical analyses of these soils as reported by Mirasol are reproduced herewith. Quanti-

ties are expressed as pounds per acre, assuming the surface $6 \frac{2}{3}$ inches to weigh 2,000,000 pounds.

Table III:- Chemical composition of soils used.

Constituents	Gray Silt Loam	Yellow Gray Silt Loam	Yellow Silt Loam
	p.p.a.	p.p.a.	p.p.a.
Nitrate Nitrogen	26	36	60
Total Nitrogen	2900	1370	1966
Phosphorus	1104	693	691
Potassium	25130	35800	29000
Calcium	4510	3920	7850
Mangesium	4520	4180	5330
Iron	47800	74200	74200
Manganese	840	786	660
Aluminium	121000	151000	14900
Lime requirement	2125	2814	2921

In addition a slightly acid brown silt loam from the University South Farm and soil from Plot 23 of the Rhode Island Agricultural Experiment Station were used for special studies. The soil of Plot 23 has received applications of ammonium sulfate since 1893 and it is extremely acid.

Experiment I

The Nature of the Aluminium Compounds Extracted with Potassium Nitrate

Using for this experiment the gray, yellow-gray, and yellow silt and the Rhode Island soils, an extract of each was made by adding to 100 gm. of soil in a 400 c.c. bottle, 250 c.c. of a normal potassium nitrate solution, shaking for three hours, and after the supernatant liquid had become perfectly clear, drawing off 125 c.c. of the solution for analysis of aluminium.

Aluminium was determined in the usual way, by precipitation with ammonium hydroxide. The precipitates were but faintly tinged with the brownish color of ferric hydroxide so that no attempt was made to separate iron from aluminium. As a check upon the results obtained by this procedure, the phenyl hydrazine method for the determination of aluminium was carried out as given by Hillebrand, (6) in Bulletin 700 of the United States Geological Survey. Practically identical results were obtained. The table below gives the results of these determinations as the average of triplicate analyses expressed in pounds per acre.

Table IV:- Aluminium in potassium nitrate extract, after three hours shaking.
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Soil	Aluminium
	p.p.a.
Gray Silt Loam	678
Yellow Gray Silt Loam	540
Yellow Silt Loam	366
Rhode Island Soil	498

These figures, of course, do not represent the total soluble aluminium of the soil since no more can be extracted after equilibrium has been established between the extractant and the soil. Fresh potassium nitrate and renewed shaking would of course bring more aluminium into solution. Aliquots of a second similar series of extracts were then pipetted into 500 c.c. collodion flasks for dialysis. These flasks were suspended in separate glass jars containing three liters of distilled water and dialysis allowed to take place for two days. During each day, water was constantly drawn off and evaporated. Finally, when one liter of the diffusate after evaporation to several cubic centimeters gave no test for nitrate with diphenylamine sulfuric acid, it was assumed that the process of dialysis was complete. The diffusate was evaporated to about 150 c.c. heated to boiling and ammonium hydroxide added until the solution was just alk-

line. No precipitate whatever of aluminium was obtained. The collodion flasks were then placed in beakers and the collodion disintegrated by digesting with strong nitric acid on a steam bath over night. Determination of aluminium showed that all of the aluminium contained in the extract had been recovered and that none had diffused through the membrane. This result points directly to the fact that all of the aluminium present in the potassium nitrate extract of the soils under study was present as the hydroxide and not as salts. These results completely confirm the work of Knight, who, as was mentioned earlier in this paper, obtained the same results by dialysis of the potassium nitrate extract of an acid soil.

Before concluding definitely that the aluminium which had been found in the potassium nitrate extracts was present as the hydroxide, it was thought desirable to make a study of the hydrosol of aluminium hydroxide, particularly with reference to its appearance, and behavior in the presence of ammonium hydroxide. Some doubt existed at this time as to whether the hydrosol would not appear quite opalescent, whereas the soil extracts were as clear as distilled water. Furthermore, it was not altogether certain that aluminium in the sol state would be precipitable by ammonium hydroxide. In order then to remove any doubts as the appearance and behavior of the sol in so far as this problem is concerned, certain observations were made on aluminium hydroxide in this condition.

Experiment 2.

Properties of the Hydrosol of Aluminium Hydroxide

The procedure followed in the preparation of the hydrosol was that of A. Muller, reproduced in Zsigmondy and Spear's Chemistry of Colloids(16). A solution of aluminium chloride containing 1.124 gm. of aluminium oxide in 50 c.c. of water was treated with ammonium hydroxide, washed quickly as possible

with water, and put into 250 c.c. of water in a flask. The whole was brought to a boil, and 20 c.c. of N / 20 hydrochloric acid added drop by drop. The hydrosol prepared in this manner was only faintly opalescent. A portion diluted with water, however, formed a perfectly clear solution. The hydrosol was found to be neutral to both red and blue litmus paper. On addition of ammonium hydroxide with warming, a gelatinous precipitate of aluminium hydroxide was formed. In view of the similarity in appearance and behavior of the aluminium hydroxide hydrosol with that form of aluminium which was found in the potassium nitrate extracts, together with the fact that the aluminium in the extracts failed to diffuse through the collodion membrane admits of no doubt as to the form in which aluminium was present in the extracts, namely as the hydrosol of aluminium hydroxide.

Experiment 3

Effect of Complete Extraction of Acidity on Nature of Aluminium Compounds in Potassium Nitrate Extracts.

The question now arose as to whether under the conditions of the extraction with consequent production of equilibrium, sufficient aluminium as salts had been extracted to give a determinable amount of aluminium after dialysis, and whether complete extraction of the soil acidity would tend to modify the character of the aluminium compounds extracted. In order then to extract the total amount of soluble aluminium in the soil, the same soils, omitting that from Rhode Island, were shaken as before with normal potassium nitrate, removing after settling all the supernatant liquid and replacing it with fresh salt solution and the shaking renewed. This process was repeated until titration of 125 c.c. of the extract required less than 0.5 c.c. of standard sodium hydroxide to neutralize it. It was found impossible to go below this figure owing to the slightly acid reaction of the potassium nitrate solution.

Six shakings of three hours each with replacement of the salt solution after the first five shakings were found to be necessary to reduce the acidity of the last portions to practical neutrality. A similar series was extracted with distilled water, but owing to the fact that two of the extracts persisted in remaining turbid, these water extracts were discarded. The results from analysis of aluminium in the potassium nitrate extracts appear below.

Table V:- Aluminium in potassium nitrate extract after complete extraction of acidity of soils.

	p.p.a.
Gray Silt Loam	1014
Yellow Gray Silt Loam	765
Yellow Silt Loam	802

A comparison of these results with those received from the single shaking with potassium nitrate reveals the fact that from one and one-half to two times as much aluminium is removed by the successive shakings as with a single shaking, which was to be expected. A very striking comparison, however, is made when the second series of results are compared with those obtained by Mirasol (reproduced in Table III, page 11) by leaching the same soils to neutrality with normal potassium nitrate. It should be noted in this connection that the procedure followed by Mirasol was quite different from that used by the writer in that the results of the former were obtained from analysis of the soils before and after extraction, no attempt being made to analyze the extract itself. And herein, undoubtedly, lies the reason for the very high results obtained by Mirasol, for it is highly probable that the percolation of the potassium nitrate through the soils carried with it mechanically a very large quantity of finely divided particles of aluminium hydroxide. Naturally the hydroxide in this form would not be found in analysis of the extract, but it would reduce enormously

the quantity of aluminium in the soil after extraction had been completed. This explanation likewise accounts for the large quantity of aluminium which Mirasol found was removed by leaching with water. None whatever could be found in the extract by the writer in repeating the work in exactly the same manner as Mirasol had done with the exception that the writer made his analysis of the actual extract rather than of the soil itself. Additional support of this result is given by the fact that the bottom of the bottles receiving the percolate was in each instance covered with a noticeable layer of finely divided material, presumably aluminium hydroxide. More detailed consideration of the water extracts will be given later.

The potassium nitrate extracts of the three soils after complete extraction were now subjected to dialysis by concentrating to small volume and dialyzing in the manner that has been described. Here another apparently abnormal result followed, for all of the aluminium contained in the extract was found to diffuse completely through the membrane and the total quantity of aluminium in the extract was recovered in the diffused portion. Treating the dialyzate with ammonium hydroxide after digestion with acid failed to give a test for aluminium.

Explanation of the Presence of Aluminium Nitrate in the Potassium Nitrate Extract.

The most obvious explanation for this phenomenon that with a single shaking of the soils with potassium nitrate only non-dialyzable aluminium was to be found in the extract, while with complete extraction only dialyzable aluminium was found must lie in the fact that the aluminium hydroxide present in the extract after shaking was converted to aluminium nitrate by the increased acidity resulting from successive shakings over a long period. It might appear possible that the single extract from the shaking contained aluminium as salts

in insufficient quantity to be detected, whereas the complete extraction removed a considerably larger amount. This contention, however, is invalidated by the fact that in the first instance non-diffusible aluminium made up the total aluminium content of the extract, whereas in the second instance the total aluminium of the extract consisted of wholly dialyzable aluminium. This fact necessarily presupposes a conversion of aluminium hydroxide to the nitrate and can hardly be explained on another basis.

Assuming such conversion to have taken place, it became necessary to ascertain whether the conversion had occurred as a result of the increased acidity, caused by the repeated shakings, or whether the concentrating of the 800 c.c. aliquots to 150 c.c. had increased the hydrogen ion concentration of the solution to a point which would convert the hydroxide to the nitrate. To settle this point, dialysis was repeated using larger collodion flasks which obviated the necessity of concentration, but complete dialysis took place as before, thus eliminating the factor of change in the nature of the aluminium compounds due to manipulation.

If the conclusion be accepted that aluminium salts were not present in the extract after the shaking of three hours, but that they were produced as a result of contact between the soil and the extract over a much longer period, then certain fundamental considerations must follow. If aluminium salts are not to be found in the extract after the shorter period of contact, then the salts cannot be the real cause of the acidity of the extract. They are produced in side reactions of the true acidic factors within the soil and diminish rather than increase the acidity of the extract to the extent that they fail to hydrolyze completely. The hydrolysis of soluble aluminium salts, on the basis of this reasoning, cannot be a contributing factor to the acidity of the soils under investigation.

A detailed consideration of the probable process by which aluminium nitrate

was produced in these soils follows. The acid soils being deficient in bases, because of their rather large content of alumino-silicic acids, alumino-silicates, organic acids and of acid salts in general, withdraw the potassium ion from the neutral salt solution until their capacity for base is satisfied. Those compounds containing aluminium then liberate this ion in proportion to the quantity of potassium absorbed. As the potassium ion is withdrawn from the potassium nitrate, hydrogen ions from the various acids and acid salts within the soil combine with the nitrate ion to form nitric acid. The nitric acid thus produced acts upon the aluminium which is replaced by potassium and forms not aluminium nitrate, as would naturally be expected, but forms the hydrosol of aluminium hydroxide. To assume that soluble aluminium hydroxide is produced under these conditions rather than aluminium nitrate probably appears out of harmony with our usual conception of chemical reactions; yet it is necessary to bear in mind the work of Rose on the formation of hydrated aluminium hydrosols in weak acid solution before the acidity is sufficient to form the normal salt. In the soil undoubtedly a series of similar hydrated hydrosols are produced until finally the concentration of nitric acid, increasing slowly by the removal of the potassium ion in the rather slow replacement reaction, reaches a point at which aluminium nitrate is produced. It is necessary to point out that contact of the salt solution with the soil over the period of two weeks during which the total extractions was made did not result in increased acidity as measured by titration, but in this period the hydrogen ion concentrations of each of the extracts rose to a point at which the hydroxide was converted to the nitrate. This is to be explained by the fact that hydrogen ions of the weakly dissociated alumino-silicic acids and organic acids which represent the total acidity of the soils, but which affect only slightly the hydrogen ion concentrations of the soil, were replaced by potassium with the result that strongly dissociated nitric acid was formed

with consequent increase in the pH value of the extracts. The data reported in Table VI substantiate this contention in that there is seen to be no increase in titratable acidity in soil extracts which have remained in contact with the soils up to three months, yet in this interval there has been a singularly large increase in the concentration of hydrogen ions in the extracts. The results reported in this table were obtained by shaking 100 gm of soil with 250 c.c. of normal potassium nitrate solution for three hours, titrating 125 c.c. immediately after settling and after standing for one and three months. Determinations of the hydrogen ion concentration of the extracts were made by the colorimetric method of Clark and Lubs (4), at the time of the titration.

Table VI:- Total titratable acidity and hydrogen ion concentration of soil extracts after contact with soil for different periods.

Soil	Time of contact of salt solution with soil	Titratable acidity c.c. of standard alkali	Hydrogen ion concentration
Yellow Silt Loam	24 hours	c.c. 11.0	pH 4.4
Yellow Gray Silt Loam	24 "	9.7	4.0
Gray Silt Loam	24 "	4.3	4.6
Yellow Silt Loam	1 month	3.0	4.2
Yellow Gray Silt Loam	1 "	9.3	4.0
Gray Silt Loam	1 "	0.6	4.6
Yellow Silt Loam	3 months	10.5	2.8
Yellow Gray Silt Loam	3 "	9.3	3.0
Gray Silt Loam	3 "	not determined	not determined

Examination of the data presented in Table VI reveals some extraordinary changes in the acidity of the soil extracts during the course of the three months standing. The hydrogen ion concentrations of the extracts have increased

considerably by the third month, pointing strongly to the production of a readily ionizable acid, in this case nitric acid. But much more striking are the changes through which the titratable acidity have passed in this period. It will be observed that the total acidity of the yellow and gray silt loams had decreased to a very marked extent after one month's standing, but after the entire period had elapsed the total acidity of each had returned to the original figures obtained by titration after 24 hours. No such change took place in the extract of the yellow gray silt loam; during the whole period, its acidity remained practically constant. Evidently chemical reactions of considerable complexity had taken place in these extracts to account for the fluctuations in the acidity, and no explanation which might be offered without further study might coincide with the actual changes which took place. Nevertheless, a possible explanation might be offered at this time which would perhaps stimulate further work along this line. It would certainly seem that some of the active hydrogen ions of the extract had been combined into compounds which removed them from the system either through the passage of the compounds into the colloidal state, e.g., silicic acid, or it may be that compounds were formed containing hydrogen which ionized to only a slight extent. Either of these possibilities would account for the reduction in acidity after one month. Such a reduction in acidity would naturally affect the hydrogen ion concentration of the extracts. Whereas, the pH value would normally rise immediately with the conversion of the weakly dissociated soil acids to the strongly dissociated nitric acid, it appears from the data presented that the reduction in total acidity from whatever cause has prevented the hydrogen ion concentration from increasing until some time after one month. After this time had elapsed, however, the constantly increasing concentration of nitric acid succeeded in bringing back into the system the acidic compounds which for some reason had been thrown out. It will be observed that the yellow gray silt loam suffers no change whatever.

Evidently it does not contain to an appreciable extent those compounds which by entering the colloidal or insoluble state reduce the acidity of the extract. Whether the explanation that has been suggested is acceptable or not does not affect the main point, namely, that for some reason there was a very considerable reduction in the total acidity of the soils during the period and subsequent return the normal acidity of the extracts. Error in manipulation cannot account for the abnormality, as a second series of aliquots from the extracts gave like results with respect to both titratable acidity and hydrogen ion concentration.

The extracts which had remained in contact with the soil for three months were subjected to dialysis with the result that the aluminium compounds in solution in the extracts diffused through the membrane, showing that in the interval of three months conversion of aluminium hydroxide to aluminium nitrate had been effected. It should be noted, however, that under the conditions of the extraction, the production of nitric acid is a reversible reaction. Removal of the products of the reaction then would be expected to accelerate its speed. This is exactly what happened in the complete extraction of the soil acidity by repeated shakings with removal of the salt solution after each shaking replacing it with fresh solution. As a result of this procedure, aluminium hydroxide was converted to aluminium nitrate within two weeks (the time required for the extraction), whereas even after one month's standing without renewal of the salt solution no such change had taken place. The hydrogen ion concentration of one of the extracts from complete extraction which happened to be saved, corresponded very closely to the pH value of the extract of the same soil after three month's standing in contact with the salt solution.

In concluding this discussion of the conversion of aluminium hydroxide to the nitrate in the potassium nitrate extracts, it is necessary to emphasize the fact the hydrolysis of soluble aluminium salts cannot possibly be a factor

contributing toward the acidity of soils in general, the term acidity being taken in its true meaning of the effect of free hydrogen ions and not including a toxic effect apart from the effect of hydrogen ions. Aluminium salts were not found to occur normally in the soils studied but were produced by the interaction of the soil acids and the potassium nitrate solution. Hence, aluminium salts are produced by soil acids and cannot therefore be a cause of the acid reaction of the soil.

Experiment 4

Aluminium in Water Extracts

Attention has been previously called to the fact that the water extracts of the soils made by repeated shakings were too turbid for use in the determination of aluminium. Any attempt to clear the extracts by flocculation of colloidal material would, of course, precipitate aluminium in the hydrosol state. Hence, percolation of the soil with distilled water was resorted to in order to obtain perfectly clear extracts. Five kilograms of each soil was placed in pots of that capacity and leached with distilled water until a 125 c.c. portion of the percolate required not more than 0.2 c.c. of standard alkali to neutralize it. Approximately 10 liters of water were required by each soil to reduce its acid reaction to neutrality.

Analysis of the water extracts for aluminium was made by evaporating aliquot portions to dryness, allowing the beakers to remain on the steam bath over night to dehydrate the silica, digesting the residue for one hour on the bath with 5 c.c. of concentrated nitric acid, diluting, and after filtering of the silica, heating to boiling and treating with ammonium hydroxide in the presence of 2 gm of ammonium chloride to faint alkalinity. No precipitate whatever formed even when 5 liter aliquots were taken of the total volume of 10 liters of each extract. When it is considered that the total quantity of soil extracted

in each case was 5000 gm.; further that there is no reason why any nitrate, sulfate or chloride of aluminium should have failed to have been removed by the water had they been present in the soil, the conclusion may be drawn with assurance that soluble aluminium was totally absent from these soils despite the fact that Mirasol has reported between 21,000 and 33,000 pounds of aluminium to have been removed from the same soils by water. The explanation for this discrepancy has been made in connection with the discussion of aluminium in potassium nitrate extracts, namely, that these figures reported by Mirasol were not secured by actual analysis of the extracts, but that they represent the loss in total aluminium of the soils after percolation had been accomplished. It was further suggested that the liquid passing through the soil had removed mechanically very fine particles of aluminium hydroxide to which the loss in aluminium may be ascribed. However, Mirasol does report results from the actual analysis of the water extracts for aluminium. These results are reproduced in Table VII.

Table VII:- Analysis of water extracts as reported by Mirasol

<u>Soil</u>	<u>Aluminium</u> mgm.
Yellow Silt	88.9
Yellow Gray Silt Loam	105.2
Gray Silt Loam	75.5

These results, however, if calculated on the acre basis vary widely from the results reported by him from analysis of the soils before and after percolation. For instance, selecting the figure given for aluminium in the first four liters of the extract of the yellow gray silt loam, namely, 105.2 mgm and calculating this in terms of pounds per acre (16 liters of water was the total volume used in leaching the soil) assuming 5000 gms to be the capacity of the pot used,

we arrive at the figure of 168 pounds per acre; whereas calculation from the results obtained indirectly i.e., by analysis of the soil before and after percolation shows that 33,400 pounds per acre had been removed. The figure 168 pounds as a matter of fact is much too large as it is computed from the quantity of aluminium in the first four liters which contained considerably more aluminium than the succeeding volumes of water.

It is now necessary to explain the reason for the discrepancy in the results of Mirasol and of the writer in direct analysis of the water extracts. Mirasol does not give his method for the determination of aluminium in the water extracts so it may be presumed that he disregarded the possible presence of soluble silica in the extracts, treating with ammonium hydroxide to precipitate aluminium directly after evaporation, instead of evaporating the extracts to dryness, dehydrating and removing the silica with subsequent treatment with ammonium hydroxide. It would seem possible then that the precipitate that he obtained with ammonia was not aluminium hydroxide but silicon hydroxide. In order to obtain experimental evidence bearing on this point, the writer evaporated four liters of each of the extracts to 200 c.c. and treated with ammonium hydroxide, white gelatinous precipitates being formed in each case. One of the precipitates was pure white, the others were tinged somewhat by ferric hydroxide. Boiling these precipitates with strong sodium hydroxide failed to dissolve them. Even boiling with fairly strong acid brought them into solution only quite slowly. The behavior of these precipitates with acid and alkali should remove any doubt that they were not aluminium hydroxide.

Resuming now further consideration of Mirasol's data concerning the presence of aluminium in ^{the} water extract, it is necessary to say first that it is utterly impossible that all of the aluminium which Mirasol succeeded in extracting from the soil by water was present as salts of the various acids. By calculation of the amount of aluminium that would be combined with the total quantity

of negative ions in the extract, assuming for the time that all of the acid ions are present as aluminium salts, it is possible to approximate the maximum quantity of aluminium that might be contained in the extract as salts. This figure compared with the total quantity of aluminium present gives the ratio of aluminium as salts to the total aluminium content. This idea has been carried out with results that appear in the table below. All of the data with the exception of the analysis of chloride and sulfate, which were carried out by the writer, are taken from Mirasol's report of his work.

Table VIII;- Acid ions of soil extracted by water with their aluminium equivalent

Ions	Gray Silt		Yellow Gray Silt		Yellow Silt	
	Acid ions	Aluminium equivalent	Acid ions	Aluminium equivalent	Acid ions	Aluminium equivalent
	p.p.a.	p.p.a.	p.p.a.	p.p.a.	p.p.a.	p.p.a.
Aluminium	-----	21,400	-----	33,400	-----	32,200
Nitrate	18	3	26	4	62	9
Chloride	152	38	212	53	112	28
Sulfate	422	79	598	112	459	86
Phosphate	*--	*--	*--	*--	13	3
Total		120		169		126

* Amount within error.

A comparison of the maximum amount of aluminium which could be combined with the total quantity of acid ions, leaving the silicate out of consideration demonstrates at once the extremely small proportion of aluminium that could be present as salts. But we know from the principles of water analysis that the acid ions are not linked with aluminium but with calcium, magnesium, potassium and sodium. All bases, in excess, are assumed to be present as hydroxides.

In no case in water analysis under normal conditions to the knowledge of the writer are acid ions ever assigned to aluminium. The only alternative to account for the large amounts of aluminium is to ascribe it to the presence of aluminium hydroxide. The writer, of course, does not lose sight of the fact that aluminium hydroxide will be generally admitted to be present in the water extract of soils; Mirasol in fact mentions its probable occurrence in the soil solution. The writer also recognizes the possibility of its presence being a potential source of toxic aluminium, but he does not admit the correctness of grouping it with aluminium in the form of salts under the head of active aluminium, i.e., aluminium that is toxic to plants. It follows, therefore, that the total of aluminium which may be found in a water extract cannot be taken as a measure of toxic aluminium since the latter occurs to the best of our knowledge only as salts which, as has been shown, are not likely to be present in soils in significant amounts.

THE PRODUCTION OF SOLUBLE ALUMINIUM IN THE SOIL BY BACTERIAL ACTIVITY

Thus far in this paper no data have been adduced which indicate that the rise of aluminium salts within the soil might contribute toward its acidity. It has been shown that aluminium salts produced by purely chemical reactions cannot possibly augment the acid reaction of the soil. It is now necessary to consider whether soil acidity might be increased by the hydrolysis of aluminium salts produced biochemically, namely, by nitrification and by sulfonation. Mirasol has emphasized the former process as being the foremost factor in the production of soluble ^{aluminium} pointing out that in absence of a more suitable base, aluminium may serve as the base in nitrification with the production of considerable quantities of aluminium nitrate. That this process may take place to any extent, however, may be doubted in view of the fact that nitrify-

ing bacteria are extremely sensitive to an acid medium which would rapidly be brought about by the hydrolysis of aluminium nitrate, if formed. Certainly nitrification could not go on appreciably under such conditions. Nevertheless, it was deemed desirable to study this question experimentally.

Experiment 5

Nitrification as a Factor in the Production of Soluble Aluminium

This experiment was performed by determining the amount of nitrate in incubated nutrient media which contained no free base which might neutralize nitric acid except aluminium hydroxide and aluminium phosphate.

The nutrient medium contained per liter of distilled water 1 gm of $K_2 HPO_4$, 0.2 gm $MgSO_4$, 1 drop of 10 percent $FeCl_3$, 1gm. of $NaCl$ and a very small amount of $CaCl_2$. 25 c.c. of the medium was poured into 500 c.c. Erlenmeyer flasks, each of which received in addition sufficient standard $(NH_4)_2 SO_4$ solution to provide 10 mg. of nitrogen. Aluminium hydroxide and phosphate were added to separate series of flasks in amounts sufficient to neutralize all of the nitric and sulfuric acids that might be produced plus a slight excess. The flasks were then inoculated with 1 c.c. of a soil infusion made by shaking 100 gm. of a black clay loam soil with 200 c.c. of water and allowing the supernatant liquid to stand until most of the soil particles had settled. Incubation at 30° was allowed to continue for four and six weeks. At the end of these intervals, the contents of the flasks were analyzed for nitrate with results as given in Table IX as averages of triplicates.

Table IX:- Nitrate production in liquid cultures

Treatment	Nitrate Nitrogen	
	4 weeks	6 weeks
	mgm	mgm
Medium, $(\text{NH}_4)_2 \text{SO}_4$	1.1	1.0
Medium, $(\text{NH}_4)_2 \text{SO}_4$, $\text{Al}(\text{OH})_3$	0.6	0.9
Medium, $(\text{NH}_4)_2 \text{SO}_4$, AlPO_4	0.5	0.5
Medium, $(\text{NH}_4)_2 \text{SO}_4$, CaCO_3	5.5	5.3

From the data contained in the above table there does not seem to be any likelihood of aluminium replacing calcium as an available base in nitrification. The experiment, however, probably does not admit of a definite conclusion on this point, since it might be that in a much longer period of incubation the aluminium compounds would slowly be attacked and a measurable quantity of nitrate would be formed. In addition, there is a possibility that if nitrification were initiated by a slight amount of carbonate, aluminium would carry on the process.

Experiment 6

The Production of Soluble Aluminium in the Soil by the Process of Sulfonation

It will be recalled that reference was made earlier in this paper to the fact that Ames and Boltz (2) report aluminium as having been rendered soluble in the process of sulfonation. As their experimental procedure did not discriminate between the two forms in which aluminium may be produced in the soil, i.e., as the hydroxide or as salts, it became necessary in order to study this problem to induce strong sulfonation in a soil and then to dialyze the

extract as in the previous experiments. Accordingly, 100 gm. portions of the yellow gray soil were placed in tumblers, 0.5 grams of sulfur was added, 0.8 grams of dried blood, and finally enough precipitated aluminium hydroxide to double the aluminium content of the soil. Water was then added to optimum moisture content and the tumblers incubated at room temperature for two months, water being added from time to time to keep the tumblers at a fixed weight. At the end of the incubation period the contents of each tumbler ^{were} transferred to a 400 c.c. shaker bottle, 200 c.c. of distilled water added and the mixture shaken for one hour. After the suspended material had settled aliquot portions were drawn from each bottle, sulfate being determined from two portions, the remainder being dialyzed in the manner that has been previously described. Very strong oxidation of sulfur was found to have taken place, the sulfuric acid formed being sufficient to increase the pH value of the soil extracts from 4 to 3. Under such conditions, it was not surprising that conversion of aluminium hydroxide to sulfate took place as was demonstrated by dialysis. It is hardly necessary to point out that the aluminium sulfate formed in this manner could not possibly have been a factor in increasing the acidity of the soil extracts since this was of course due solely to the sulfuric acid formed.

Experiment 7

The Influence of Aluminium Salts on Ammonification and Nitrification

Although thus far in the experimental work that has been reported in this paper, no evidence has been adduced that has indicated the presence of aluminium salts in acid soils under normal conditions; yet we are confronted with the results of the work of Hartwell and Pember (11) which seems to admit of no other conclusions than that aluminium was the toxic factor which accounted for the unique difference in the response of rye and barley to identical soil

conditions. Other work which hardly need be reviewed at this time points quite clearly to the harmful influence of those salts in acid soils. Acid soils under a given set of conditions as in sulfonation may favor the production of aluminium salts; and although the absolute quantity of salts produced at any one time may be very small, yet owing to their very high toxicity, plant growth might be seriously affected.

With these considerations in mind and in view of the lack of data in the literature bearing on the influence of aluminium salts on ammonifying and nitrifying organisms, it was deemed advisable to study to what extent the soil flora concerned in nitrate production reacts toward toxic aluminium. Data which would demonstrate the relative toxicity of the aluminium salts likely to occur in the soil seemed of sufficient importance to warrant some attention being given to this phase of the subject, also. Furthermore, if aluminium was found to inhibit seriously the normal functioning of the nitrifying organisms, it would be of considerable practical importance to ascertain the relative value of certain common fertilizing materials in inactivating the toxic aluminium. A description of the experiments devised to throw light on these points follows.

The soil selected for this work was a slightly acid brown silt loam from the University South Farm. Its lime requirement according to the Hopkins' method was 300 pounds per acre. Having a high ammonifying and nitrifying power it was for this reason more suitable than any of the acid soils used in connection with the work on extraction of aluminium. An obvious objection to the use of a soil of such a slight degree of acidity is that aluminium applied to it as salts would be precipitated until the acidity of the salts had increased the hydrogen ion concentration of the soil beyond the point at which aluminium is thrown out of solution. However, it was planned to apply the aluminium salts over a sufficiently wide range of concentration that no difficulty would be

experienced in bringing about, for the duration of the experiment at least, the presence of soluble aluminium in the soil. Time did not permit a complete chemical analysis of the soil, but for the sake of information an analysis is presented in the table below which represents the average chemical composition of the soil of the same type in the county from which the sample was taken. This data was obtained from the Soil Report of Champaign county, Illinois, prepared by the University of Illinois.

Table X:- Composition of brown silt loam of Champaign county

(Figures represent average pounds per acre in 2 million pounds of surface soil to a depth of 6 $\frac{2}{3}$ inches)			
	Constituent	p.p.a.	
	Total Nitrogen	4,670	
	" Phosphorus	1,060	
	" Potassium	35,430	
	" Magnesium	9,550	
	" Calcium	10,680	

One hundred gram- portions of the soil were placed in tumblers and mixed with organic matter consisting of a mixture of alfalfa and sweet clover residues and furnishing nitrogen equivalent to 200 pounds per acre. The nitrate, of aluminium chloride, sulfate and phosphate were then applied to separate series in chemically equivalent amounts. The concentrations of salts appear in the table to follow. With the exception of the phosphate all of the salts were added in solution. Water was added in amounts such that the total volume of liquid applied, that is, water and the aluminium salt solution, was 25 c.c., the optimum moisture content of the soil. This moisture content was maintained as nearly as possible during the incubation period by adding from time to time the amount of water

lost from several weighed tumblers. The experiment consisted of four series, namely ammonia production in one week and two weeks, and nitrate production in one and two months incubation. The results reported are averages of the analyses of duplicate tumblers. Whenever difficulty was met in obtaining satisfactory checks that section of the work was repeated. Ammonia was determined by distilling with magnesium oxide, nitrate by boiling of ammonia with sodium peroxide and distilling with Devarda alloy.

Table XI:- Concentration of aluminium salts used.

Number	Fraction of Molecular weight per 100 gms soil	$\text{Al}(\text{NO}_3)_3$	AlCl_3	$\text{Al}_2(\text{SO}_4)_3$	AlPO_4
		p.p.a.	p.p.a.	p.p.a.	p.p.a.
1	156×10^{-7}	67	42	107	38
2	625×10^{-7}	266	167	427	153
3	25×10^{-5}	1064	669	1709	610
4	1×10^{-3}	4255	2688	6836	2440
5	4×10^{-3}	17,019	10,670	27,348	9759

Table XII:- Ammonia production in soil after 1 and 2 week's incubation

Concentration: $\text{Al}(\text{NO}_3)_3$		AlCl_3		$\text{Al}_2(\text{SO}_4)_3$		AlPO_4	
Number	1 week 2 weeks	1 week 2 weeks	1 week 2 weeks	1 week 2 weeks	1 week 2 weeks	1 week 2 weeks	1 week 2 weeks
	p.p.a.	p.p.a.	p.p.a.	p.p.a.	p.p.a.	p.p.a.	p.p.a.
Check	24 23	24 23	24 23	24 23	24 23	24 23	24 23
1	29 16	29 20	36 26	34 28			
2	27 16	30 16	32 24	30 24			
3	40 18	30 19	32 21	28 16			
4	36 20	39 58	26 12	32 24			
5	33 34	40 36	21 0	50 23			

Table XIII - Nitrate production in soil after
1 month's incubation

Concentration		Al(NO ₃) ₃			AlCl ₃	Al ₂ (SO ₄) ₃	AlPO ₄
		Total	applied as Al(NO ₃) ₃	Recovered			
		p.p.a.	p.p.a.		p.p.a.	p.p.a.	p.p.a.
Check		126	--	126	126	126	126
1		185	12	173	33	141	90
2		84	48	36	33	111	135
3		174	192	--	96	90	135
4		173	768	--	48	72	174
5		159	2,072	--	54	174	204

Table XIV:- Nitrate production in soil after
2 month's incubation

Concentration		Al(NO ₃) ₃			AlCl ₃	Al ₂ (SO ₄) ₃	AlPO ₄
		Total	applied as Al(NO ₃) ₃	Recovered			
		p.p.a.	p.p.a.		p.p.a.	p.p.a.	p.p.a.
Check		54	--	54	54	54	54
1		82	12	72	72	110	90
2		90	48	42	66	99	60
3		114	192	--	72	62	48
4		201	768	--	72	93	78
5		336	3,072	--	60	76	lost

Discussion of Results from Ammonification and Nitrification

Considering first the ammonia determinations after one week's incubation, we may say that no toxic effect is to be noted; as a matter of fact, a considerable stimulation seems to be the rule even in the very high concentrations. No great depression of ammonia takes place after two weeks except in the two highest concentrations of aluminium sulfate and in a few other cases. These variations may be explained by the fact that nitrate production was stimulated at these particular concentrations, a fact which is borne out in part by the nitrate data.

Turning now to the data of nitrate production after one month we find as might have been predicted from our knowledge of the sensitivity of the nitrite and nitrate organisms to acidity that, with the exception of the phosphate in which there is stimulation, there is a general decrease in nitrate formed with increasing concentrations of the salts. The high result in the fifth concentration of aluminium sulfate is probably to be explained by a disturbance in the system brought about by the high acidity. No doubt the aluminium has exerted its toxic effect as in the other concentrations, but this effect is masked by the dissolving out of some elements to which the bacteria readily responded. The results from the applications of aluminium nitrate are altogether unsatisfactory because none of the nitrate applied in the higher concentrations could be recovered after incubation. Apparently the conditions were favorable for the rapid development of a nitrate consuming flora, or denitrification may have taken place. It was predicted that the phosphate would probably not exert a toxic effect, and it was incorporated in the series partly with the idea in mind of finding whether the nitrifying bacteria would respond to quite insoluble phosphate. Then, it was reasoned, if the phosphate ion is removed by the organ-

isms, the free aluminium ion may have opportunity to exert a toxic effect by combining with an acid radical. The phosphate, it would seem, is quite available to bacteria.

The nitrate results after two months' incubation are quite striking in that they demonstrate the fact that soluble aluminium is slowly precipitated or thrown out of action in some way by the soil even in the very highest concentrations. It is realized, as has been indicated before, that a soil of this character would likely dispose of considerable active aluminium by precipitation, and for this reason the objection might be raised that the results are not applicable to normally acid soils. Yet, if this soil is able to dispose of some 27,000 pounds of aluminium sulfate and 10,000 of aluminium chloride, it would seem that a more acid soil could inactivate the much smaller quantities of aluminium salts that it is likely to contain.

For some unknown reason the magnitude of the results from the two month's incubation is lower than that from the incubation of a single month. Possibly denitrification resulted from an excess of water that might have been added during the course of the incubation period, or it may be that after the maximum quantity of nitrate had been produced, a considerable quantity of nitrate was utilized by a strong nitrate consuming flora. The general trend of the data, however, is not affected by the rather low production of nitrate in the longer incubation period.

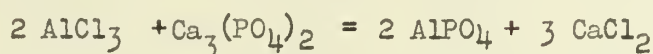
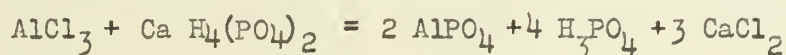
Experiment 8

The Influence of Fertilizing Materials on the Precipitation of Aluminium.

The final experiment to be reported has to do with the relative efficiency of certain fertilizer materials, namely, calcium carbonate, monocalcium phosphate and tricalcium phosphate in diminishing the toxicity of aluminium.

Each of these compounds was mixed with soil in the amounts necessary to precipi-

tate the aluminium from aluminium chloride which was added to the soil in the same concentrations that were employed in the previous experiments. The precipitation of the aluminium from aluminium chloride was assumed to take place according to the following equations:



Incubation was allowed to take place for one month. The results with tricalcium phosphate was unsatisfactory so that a second series was incubated. The results from this second series with tricalcium phosphate should be compared with the results from the aluminium chloride series which accompanied it rather than with the results of the first series. Chemically pure chemicals were used.

Table XV:- Effect of carbonate and phosphates in inactivating soluble aluminium, as measured by nitrate production. Results expressed in pounds per acre of nitrate nitrogen.

Concentration	AlCl_3	$\text{AlCl}_3 + \text{CaCO}_3$	$\text{AlCl}_3 + \text{CaH}_4(\text{PO}_4)_2$	
	p.p.a.	p.p.a.	p.p.a.	
0	126	126	126	
1	63	186	78	
2	63	183	108	
3	96	153	102	
4	48	172	84	
5	54	87	36	

Table XVI:-Effect of carbonate and phosphates in inactivating aluminium salts(continued)

Series 2

Concentration	AlCl_3 alone	$\text{AlCl}_3 + \text{Ca}_3(\text{PO}_4)_2$	
0	p.p.a. 120	p.p.a. 120	
1	108	126	
2	93	105	
3	66	92	
4	105	99	
5	75	30	

The superiority of calcium carbonate over the two phosphates precipitating aluminium is apparent at once. The monocalcium phosphate is likewise to be preferred to the tricalcium phosphate for this purpose.

The inferiority of the monocalcium phosphate to calcium carbonate in the precipitation of aluminium as judged by nitrate production is in direct contrast to the conclusion of Hartwell and Pember, and Conner who report the great effectiveness of acid phosphate in neutralizing the toxicity of aluminium. The fact, however, that these investigators did not use nitrate production as the criterion for their conclusions may perhaps account for their preference.

IV. SUMMARY

The experimental work that has been reported, together with the interpretations of which it admits, have established conclusively the fact that aluminium salts were not present in the acid soils which were used in this investigation. Although aluminium nitrate was found in the potassium nitrate extract

of the soils after complete extraction of the acidity had been accomplished, this fact by no means establishes the normal occurrence of aluminium salts in these soils. The very fact that not a trace of soluble aluminium was found in the water extracts is conclusive evidence of its absence, as there is no reason why salts of aluminium, if present, should not have been extracted by distilled water. It has been shown further that even if the total content of acid ions within the soil were combined with aluminium, even this impossible condition could account for only an insignificant quantity of aluminium.

Soluble aluminium salts may be produced in acid soils by the action of the mineral acids formed by removal of the basic ions of sulfates, chlorides and nitrates upon aluminium hydroxide. The basic ions replace aluminium in certain soil minerals, the aluminium coming into solution as the hydroxide. With increasing hydrogen ion concentration of the soil solution, brought about by the production of highly ionized acids by withdrawal of the bases from salts, a point is reached when aluminium hydroxide in solution is converted into soluble aluminium salts. Since the hydrolysis of these salts cannot increase the acidity of the soil beyond the degree of acidity existing at the time of their formation, the conclusion may be definitely drawn that aluminium salts are not a factor in the acidity of soils, taking the term acidity to refer to the effect of free hydrogen ions and not including a toxic effect due to other causes. Rather than causing an acid condition in soils, aluminium salts are themselves produced by the acidity of the soil, and hence cannot contribute toward it.

It has been shown that the presence of soluble aluminium salts stimulates ammonification while nitrification proper is affected adversely with increasing concentration of the salts. This inhibitive effect, however, obtained in the soil used only for a relatively short time, perhaps no longer than a month. After two month's incubation it is striking to note that, with nitrate production as the criterion, the soluble aluminium had been rendered inactive. Calcium car-

bonate was shown to be more effective than either monocalcium or tricalcium phosphate in precipitating aluminium.

V. CONCLUSIONS

1. Soluble aluminium salts were not found to be present in the soils used in this investigation.
2. Aluminium salts, although perhaps occurring in some acid soils, do not contribute to the acidity of the soils, but are themselves produced as side reactions in the action of the soil acidity.
3. Aluminium salts are stimulating to ammonifying organisms, but act adversely upon nitrate bacteria in soil. This effect, however, is temporary only, as an acid soil seems to have considerable capacity for inactivating toxic aluminium.
4. Calcium carbonate is the most effective soil amendment in preventing toxic action of aluminium salts on nitrification.

VI. ACKNOWLEDGMENT

The writer takes pleasure in expressing his appreciation to Dr. A.L. Whiting for many helpful suggestions and much valuable criticism.

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